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(54) TITLE OF THE INVENTION

Electron Beam-Hardening Adhesive and Polyester Film Laminated Metal Plate Making Use Thereof

(57) ABSTRACT

PURPOSE

To obtain an adhesive layer which can be used for a long period of time to manufacture a PET laminate metal plate with excellent blocking resistance, and favorable adhesion, processability, and retort resistance.

RESOLUTION MEANS

An electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight to arithmetic mean molecular weight ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g;

and also a polyester film laminated metal plate wherein a polyester film which may have an ink layer is laminated using said adhesive.

EXTENT OF PATENT CLAIMS

What Is Claimed Is:

Claim 1

An electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g.

Claim 2

The electron beam-hardening adhesive according to Claim 1, further containing between 2 and 10 weight parts of unblocked polyisocyanate compound and between 0 and 20 weight parts of blocked polyisocyanate compound in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 3

The electron beam-hardening adhesive according to Claim 1 or Claim 2, further containing between 1 and 50 weight parts of an antiblocking agent in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 4

The electron beam-hardening adhesive according to any one of Claims 1 through 3 further containing between 50 and 250 weight parts of white pigment in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 5

A polyester film laminated metal plate made by laminating a polyester film which may have an ink layer onto one or both sides of a metal plate using said electron beam-hardening adhesive shown in Claim 1.

Claim 6

A manufacturing method for a polyester film laminated metal plate comprising:

(1) a step of applying and drying said adhesive shown in Claim 1 onto a polyester film (A) which may have an ink layer;

(2) a step of rolling the polyester film having a dried adhesive layer into a coil; and

(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

Claim 7

The manufacturing method for a polyester film laminated metal plate according to Claim 6, further comprising (4) a step of hardening the adhesive layer by irradiating an electron beam onto the thermocompressed adhesive layer.

DETAILED DESCRIPTION OF THE INVENTION

[0001] TECHNICAL FIELD OF THE INVENTION

The present invention relates to an electron beam-hardening adhesive which can form an adhesive layer for a polyester film laminate metal plate with excellent appearance, adhesion to the metal plate, blocking resistance, and can be used for long period of time, as well as to a polyester film laminate metal plate which uses said electron beam-hardening adhesive and to a manufacturing method for said laminate metal plate.

[0002] BACKGROUND TECHNOLOGY AND PROBLEM TO BE RESOLVED BY THE INVENTION

Conventionally, metal plate which has been laminated with a polyester film which is used for cans for beverages and cans for food (hereinafter referred to as "PET laminate metal plate") normally consists of a metal plate overlaid with a polyester film using an adhesive (for instance, refer to Japanese Unexamined Patent Application H3-87249, and the like).

[0003] A conventional PET laminate metal plate, for instance, is made by (1) a step of printing ink, if necessary, on a polyester film which is a transparent plastic film, drying, applying an adhesive thereon, and then drying until tack-free (normally at approximately 50°C to 150°C for several seconds); or (2) a step of hardening by heating (normally at approximately 160°C to 170°C for approximately 0.5 seconds) and compressing a polyester film onto which an adhesive layer has been formed, onto a metal plate.

[0004] However, the aforementioned conventional manufacturing method has the following problems.

[0005] 1. In order to meet conditions for manufacturing PET laminate metal plate using a high-speed production line necessary for large volume production, the baking oven must be lengthened and this equipment is large so the equipment expense will increase and more plant space will be required.

[0006] 2. With a conventional manufacturing method, if the lamination speed exceeds 150 m/min, or if the lamination temperature is below 160°C, areas without sufficient adhesion will appear, and variations in appearance will easily occur.

[0007] 3. A can for beverages or a can for food manufactured from PET laminated metal plate obtained by a conventional method has poor processing properties (necking process, flanging process, beading process, and the like) and because of the heat from baking (maximum temperature between 230°C and 280°C for between approximately 7 and 100 seconds) the side seam paint (paint for repairing the weld region) and the heat of welding at the can body seam line in the area of the weld, whitening or blistering may occur after retort processing, a pattern similar to water spots may appear on the surface of the polyester film, and surface finish will readily be degraded because of reduced gloss, and the like.

[0008] In order to resolve the aforementioned problems, the present inventors have previously proposed in Japanese Unexamined Patent Application H6-192637 a method for obtaining a film laminated metal plate using an electron beam hardened adhesive as the adhesive, and after laminating a polyester film having an ink layer onto a metal plate using the electron beam-hardening adhesive, an electron beam is irradiated through the polyester film in order to harden the adhesive.

[0009] The aforementioned problems can be resolved by the method according to this proposal. However, the aforementioned polyester film laminated with an ink layer and an adhesive layer (hereinafter also abbreviated as "lamination film") is normally rolled in a coil after the adhesive is dry, stored until the time of use, and then uncoiled and applied to a metal plate at the time of use, but the lamination film according to the aforementioned proposal experiences large changes in the degree of hardness of the adhesive layer during storage and the adhesive forces between the adhesion layer and the metal plate may be weakened depending on the hardness, so there is a problem that the time period when the lamination film can be laminated to the metal plate is short. Furthermore, if an attempt is made to minimize the change in the degree of the hardness of the adhesive layer to lengthen the period that lamination is possible, of the short period after the lamination film is produced, if the film is laminated to the metal plate within, for instance, five days, appearance defects will easily occur due to wrinkling of the film, and problems with adhesive protruding out from the film surface will easily occur, so there is a problem that favorable lamination cannot be performed until after at least five days have passed as a curing period after the lamination film is produced, and thus the period that the lamination film can be used is severely restricted.

[0010] The present inventors have performed diligent research to obtain an adhesive which can resolve the aforementioned problems, can form a favorable laminate after approximately 1 day after the film is manufactured, and can form a laminate even after more than three months has passed after the laminate film was manufactured, such that a PET laminate metal plate made by laminating this laminate film onto a metal plate will have excellent performance for a PET laminate metal plate such as appearance, processability, adhesion between the polyester film and metal plate, and retort resistance.

[0011] As a result, the present inventors have discovered that the aforementioned objectives can be achieved by an electron beam-hardening adhesive consisting of specific polyester resins modified with polybasic groups and polymeric unsaturated oligomer, and have thus achieved the present invention.

[0012] MEANS FOR RESOLVING PROBLEMS

In other words, the present invention provides an electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g.

[0013] Furthermore, the present invention provides a polyester film laminated metal plate made by laminating a polyester film which may have an ink layer onto one or both sides of a metal plate using said electron beam-hardening adhesive.

[0014] Moreover, the present invention provides a manufacturing method for a polyester film laminated metal plate comprising:

(1) a step of applying and drying said electron beam-hardening adhesive on to a polyester film which may have an ink layer;

(2) a step of rolling the polyester film having a dried adhesive layer into a coil; and

(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

[0015]

PREFERRED EMBODIMENTS

The electron beam-hardening adhesive of the present invention will be described below in greater detail.

[0016] The adhesive of the present invention contains as essential components polyester resin (a) and polymeric unsaturated oligomer (b).

[0017] Polyester resin (a)

The polyester resin (a) is a polyester resin obtained by an ester reaction between a polybasic acid and a polyester prepolymer containing hydroxyl groups which is an esterified compound with a polybasic acid component and a polyhydric alcohol component as the main raw material components.

[0018] The polyester resin (a) suitably has an arithmetic mean molecular weight of between 10,000 and 40,000, preferably between 12,000 and 22,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, preferably between 3.0 and 6.2, a glass transition temperature between 20°C and 55°C, preferably between 20°C and 40°C, a hydroxyl value of between 3 and 25 KOH mg/g, preferably between 5 and 15 KOH mg/g, and an acid value between 5 and 30 KOH mg/g, preferably between 8 and 20 KOH mg/g.

[0019] For the polyester prepolymer with hydroxyl groups used to manufacture the polyester resin (a) the polybasic acid component which is a main raw material component of the prepolymer is one or more types of dibasic acids selected from phthalic anhydride, iso-phthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, fumaric acid, adipic acid, azelaic acid, subacid acid, decanedioic acid, maleic anhydride, itaconic acid, and dimer acid, and the like, as well as lower-level alkyl esters of these acids, and, if necessary, may be used in combination with polybasic acids with a hydroxyl value of 3 or higher, such as trimellitic anhydride, methylcyclohexene tricarboxylic acid, pyromellitic anhydride, and the like.

These polybasic acid components may be used individually, or two or more types may be blended and used. Furthermore, if necessary, a monobasic acid such as benzoic acid, crotonic acid, p-t-butyl benzoic acid, or the like, may be used in addition to the aforementioned polybasic acid components.

[0020] The polyhydric alcohol component which is a main raw material component of the polyester prepolymer with hydroxyl groups is primarily consisting of dihydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, neopentyl glycol, 3-methylpentanediol, 1,4-hexanediol, 1,6-hexanediol, cyclohexanedimethanol, hydrogenated bisphenol A, ethylene oxide adducts of bisphenol A, and propylene oxide adducts of bisphenol A, and if necessary, polyhydric alcohols with a value of 3 or higher such as trimethylolethane, trimethylolpropane, and pentaerythritol, or the like, may also be used in combination. These polyhydric alcohols may be used individually, or two or more types may be blended and used.

[0021] The esterification reaction or ester substitution reaction between the aforementioned acid components and the polyvalent alcohol components may be performed using a previously known method; and, for instance, can be performed by polymeric condensation of the acid component and polyhydric alcohol component at a temperature of between approximately 180°C and 250°C.

[0022] The polyester prepolymer with hydroxyl groups obtained as described above has an arithmetic mean molecular weight between 9000 and 39,000, preferably between 11,000 and 21,000, and should have a hydroxyl value in a range between 8 and 45 KOH mg/g.

[0023] The polyester resin (a) can be manufactured by causing an addition reaction to occur between the polyester prepolymer with hydroxyl groups obtained as described above with a polybasic acid such as maleic acid, maleic anhydride, phthalic anhydride, trimellitic anhydride, adipic acid, azelaic acid, and dimer acid, or the like, partially esterifying a portion of the hydroxyl groups in the prepolymer, and introducing carboxyl groups. The polybasic acid used in the aforementioned partial esterification reaction is preferably an acidic anhydride. The partial esterification reaction may be performed by a previously known method, and, for instance, can be achieved by reacting the aforementioned polyester prepolymer with hydroxyl groups and a polybasic acid anhydride at a temperature between approximately 170°C and 190°C.

[0024] With the adhesive of the present invention, the polyester resin (a) may be one type of resin, or two or more may be blended and used together.

[0025] Polymeric Unsaturated Oligomer (b)

The polymeric unsaturated oligomer (b) has at least one, preferably between 2 and 4 polymeric unsaturated double bonds in each molecule, and the polymeric unsaturated double bonds are present in a concentration of between 5 and 15 mol/kg, preferably between 5 and 10 mol/kg, have an arithmetic mean molecular weight between 200 and 2000, preferably between 300 and 1500, and a hydroxyl value between 0 and 200 KOH mg/g, preferably between 30 and 80 KOH mg/g.

[0026] The type resin of the polymeric unsaturated oligomer (b) is not particularly restricted, and for instance, modified polyester resin, acrylic resin, modified urethane resin, modified epoxy resin, and the like, may be suggested.

[0027] The aforementioned modified polyester resin oligomer may be obtained, for instance, by ester bonding a polymeric unsaturated carboxylic acid such as acrylic acid with a low molecular weight polyester that has hydroxyl groups and that has an arithmetic mean molecular weight of approximately 1900 or less, in order to introduce polymeric double bonds. The aforementioned low molecular weight polyester containing hydroxyl groups can be obtained by polymeric condensation to a molecular weight within the aforementioned range using as the main raw materials the polyhydric alcohol component and polybasic acid component that were used when manufacturing the polyester prepolymer containing hydroxyl groups used to manufacture the aforementioned polyester resin (a). Commercial examples of modified polyester resin oligomer include Aronix M-7100, Aronix M-8100, and Aronix M-9050 (product names, product of Toagosei Co., Ltd.).

[0028] The aforementioned acrylic resin oligomer may be obtained, for instance, by reacting a low molecular weight acrylic resin that has functional groups such as hydroxyl groups, carboxyl groups, or epoxy groups, or the like, and that has an arithmetic mean molecular weight of approximately 1900 or less, with a polymeric unsaturated compound containing reactive groups that have polymeric unsaturated groups and reactive groups that are reactive towards the functional groups in the acrylic resin, under conditions such that the polymeric unsaturated groups are not eliminated, in order to introduce polymeric double bonds to a low molecular weight acrylic resin. Commercial examples of the aforementioned acrylic resin oligomer include Aronix M-305, and Aronix M-450 (product names, product of Toagosei Co., Ltd.).

[0029] The modified urethane resin oligomer can be obtained, for instance, by first reacting ethylene oxide with isocyanuric acid to introduce hydroxyl groups, and then reacting this isocyanurate acid which contains hydroxyl groups with a polymeric unsaturated compound which contains functional groups that are reactive towards the hydroxyl groups such as polymeric unsaturated compounds containing carboxyl groups such as acrylic acid in order to introduce polymeric unsaturated groups. Commercial examples of the aforementioned modified urethane resin oligomer include Aronix M-315, and Aronix M-215 (product names, product of Toagosei Co., Ltd.).

[0030] The modified epoxy resin oligomer can be obtained, for instance, by reacting a polymeric unsaturated compound containing carboxyl groups such as acrylic acid, or the like, with a compound containing at least one, preferably two or more epoxy groups, in order to introduce polymeric unsaturated groups.

[0031] With the adhesive of the present invention, the polymeric unsaturated oligomer (b) may be one type of resin, or two or more may be blended and used together.

[0032] With the adhesive of the present invention, the formulation amount of polymeric unsaturated oligomer (b) is suitably in a range between 3 and 30 weight parts, preferably in a range between 5 and 15 weight parts in 100 weight parts of the aforementioned polyester resin (a) from the viewpoint of hardness, adhesion, and blocking resistance.

[0033] The adhesive of the present invention contains as essential components the aforementioned polyester resin (a) and the polymeric unsaturated oligomer (b), and may consist of polyester resin (a) and polymeric unsaturated oligomer (b), but for the purpose of improving the application productivity of the adhesive, normally an organic solvent is added, and if necessary, for instance, hardening agents, hardening catalysts, anti-blocking agents, colored pigments, lubrication enhancers, silane coupling agents, defoaming agents, and antistatic agents, and the like, may be appropriately added.

[0034] The aforementioned organic solvents are substances which can dissolve or disperse the adhesive composition, and examples include hydrocarbon-based solvents such as toluene, xylene, and Solvesso #150 (product of Esso Petroleum, high boiling point hydrocarbon-based petroleum solvent), ketone-based solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, and ester-based solvents such as ethyl acetate, butyl acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monoethyl ether acetate, and the like, and one or more of the solvents may be suitably selected and used.

[0035] The aforementioned hardening agent is a substance which can cause the adhesive to harden when heated by reacting with the polyester resin (a) or in some cases with the polymeric unsaturated oligomer (b), and for example, polyisocyanate compound and amino resins, or the like, may be suggested, but of these, polyisocyanate compounds are suitable from the viewpoint of adhesion with the PET film surface.

[0036] The aforementioned polyisocyanate compound may be an unblocked polyisocyanate compound where the isocyanate groups are unblocked, or may be a block polyisocyanate compound where at least one of the isocyanate groups in the molecule are blocked, and a mixture of these is also acceptable.

[0037] Specific examples of the aforementioned unblocked polyisocyanate compounds include aliphatic diisocyanates such as hexamethylene diisocyanate and trimethyl hexamethylene diisocyanate; cyclical aliphatic diisocyanates such as hydrogenated xylylene diisocyanate, isophorone diisocyanate; aromatic diisocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate; and polyisocyanate compounds which have three or more isocyanate groups such as triphenylmethane-4,4',4"-triisocyanate, 1,3,5-triisocyanate benzene, 2,4,6-triisocyanate toluene, 4,4'-dimethyl diphenylmethane-2,2',5,5'-tetraisocyanate, and other organic polyisocyanates, in an unmodified condition or as an adduct between these organic polyisocyanate and a polyhydric alcohol, low molecular weight polyester resin, or water, or the like, as well as cyclical compounds of the aforementioned organic polyisocyanate compounds with other organic polyisocyanate compounds, and also isocyanate biurets. Of these, an isocyanate that is a cyclopolymer of hexamethylene diisocyanate is preferable for use.

[0038] The blocked isocyanate compound is an isocyanate wherein at least one of the isocyanate groups of the aforementioned polyisocyanate compound molecules is blocked by a blocking agent, and has at least one blocked isocyanate group in the molecule, but may or may not have blocked isocyanate groups. **[Translator's Note: Possible mistake in the Japanese. Probably should read "but may or may not have unblocked isocyanate groups."]**

[0039] Examples of the aforementioned blocking agents include phenols such as phenol, cresol, and xylenol; lactams such as epsilon caprolactam, delta-valerolactam, gamma-butyrolactam, and beta-propiolactum; alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether and benzyl alcohol; oximes such as formamidoximes, acetoaldoxime, acetoxime, methylethyl ketoxime, diacetylmonoxime, benzophenone oxime and cyclohexane oxime; active methylenes such as dimethyl malonate, diethyl malonate, ethyl acetoacetate, methyl acetoacetate, and acetylacetone, and the like. Of these, oxime blocking agents are most suitably used.

[0040] If a hardening agent is added, the formulation amount is preferably within a range below 30 weight parts in a total of 100 weight parts of the aforementioned components (a) and (b).

[0041] If a polyisocyanate compound is used as the hardening agent, a range of between 2 and 10 weight parts of unblocked polyisocyanate compound and a range between 0 and 20 weight parts of blocked polyisocyanate compound in a total 100 weight parts of the aforementioned component (a) and component (b) is suitable. By using both unblocked polyisocyanate compound and block polyisocyanate compound as the hardening agent, normally a balance can easily be achieved between hardness, lamination at high speed, and length of time that the PET film can be used.

[0042] The aforementioned hardening catalyst added in order to promote the reaction of the hardening agent, and if the hardening agent contains blocked polyisocyanate compound, organic metal catalysts such as tin octylate, dibutyltin di(2-ethylhexanoate), dioctyltin di(2-ethylhexanoate), dibutyltin dilaurate, dibutyltin oxide, dioctyltin oxide, and lead 2-ethylhexanoate, or the like, may be suitably used. If a hardening catalyst is added, the formulation amount is preferably within a range between 0.01 and 5 weight parts in a total of 100 weight parts of the aforementioned component (a), component (b), and a hardening agent.

[0043] The aforementioned antiblocking agent may be added, if necessary, in order to prevent adhesion and blocking from occurring between the adhesive layer and the adhesive-free surface of the PET film where an adhesive was not applied, which causes uncoiling to be difficult when an adhesive is applied to a PET film and the dried laminate film for laminating the metal plate is rolled in a coil and then uncoiled, or to prevent the adhesive from adhering to the PET film surface when being uncoiled.

[0044] Examples of the aforementioned antiblocking agent include body pigments such as fine silica powder, barium sulfate, calcium carbonate, talc, mica, and clay; polyolefin fine particles such as polyethylene fine particles, acid modified polyethylene fine particles, maleinized polypropylene fine particles, and polypropylene fine particles; and organic resin fine particles such as nylon fine particles, acrylic resin fine particles, silicone rubber fine particles, urethane resin fine particles, phenol resin fine particles, and polytetrafluoroethylene fine particles, and the like. The aforementioned organic resin fine particles have an average particle diameter of between 0.1 and 40 μm, preferably between 1 and 10 μm, and the softening point is preferably in a range between 100 and 200°C, and the resin type is most preferably polyethylene, polypropylene, or nylon.

[0045] If the aforementioned antiblocking agents are added, the formulation amount is normally within a range between 0.1 and 50 weight parts in a total of 100 weight parts of the aforementioned polyester resin (a) and polymeric unsaturated oligomer (b), and if the antiblocking agent is a body pigment, a range between 10 and 50 weight parts is preferable, in a range between 10 and 40 weight parts is more preferable, but if the antiblocking agent is organic resin particles, a suitable amount is between 0.1 and 30 weight parts, more preferably within a range between 1 and 20 weight parts. If the amount of antiblocking agent added is too high, the thermal softening of the adhesive layer will be reduced and the adhesive force between the PET film adhesive and the metal plate will be reduced, and lamination may not be possible, and furthermore, when the PET laminated metal plate or formed part thereof is subjected to retort processing, the PET film will easily peel from the metal plate.

[0046] The aforementioned colored pigment may be a white pigment such as titanium oxide, or a different colored pigment, or a glitter pigment such as aluminum powder. If the PET laminate metal plate is used as the outside surface of a can, normally multicolor printing is performed and a colored layer (normally a white coat) is required under the printing ink layer, but if an adhesive with a colored pigment and particularly a white pigment is used, the adhesive may also act as a white coat, and therefore one step of the can manufacturing process can be eliminated, which is extremely advantageous. The amount of colored pigment added is not particularly restricted so long as the level is within a range which does not hinder the performance of the adhesive layer, and normally, a quantitative range below 250 weight parts in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b) is appropriate, and for white pigments, normally a range between 50 and 250 weight parts is preferable.

[0047] The aforementioned lubrication-enhancing agent is added to provide lubrication to the surface of the adhesive, and is added in order to allow smooth coiling of the adhesive coated lamination film for laminating metal plate, and to prevent sticking of the adhesive layer surface when the coil is unrolled. Examples of the lubrication-enhancing agent include aliphatic ester waxes; polyolefin waxes such as polyethylene wax; animal waxes such as lanolin or beeswax; plant waxes such as carnauba wax and water wax, and other waxes such as microcrystalline wax, silicon wax, and fluorine wax, and the like.

If a lubrication-enhancing agent is added, the formulation amount is preferably within a range between 0.01 and 10 weight parts in a total of 100 weight parts of the aforementioned components (a) and (b).

[0048] The aforementioned electron beam-hardening adhesive of the present invention is particularly suitable as an adhesive for use in polyester film laminated metal plates.

[0049] The polyester film laminated metal plate of the present invention has a polyester film which may have an ink layer laminated onto one or both sides of a metal plate using the adhesive layer. The adhesive layer must be electron beam hardened by the final product stage, but at the stage of the polyester film laminated metal plate, the adhesive layer may be, but is not required to be, electron beam hardened.

[0050] Next, the manufacturing method for the polyester film laminate metal plate will be described in detail.

[0051] The manufacturing method for the polyester film laminate metal plate of the present invention is comprising:
(1) a step of applying and drying the electron beam-hardening adhesive of the present invention onto a polyester film which may have an ink layer;
(2) a step of rolling the polyester film (A) having a dried adhesive layer into a coil; and
(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

[0052] The polyester film (A) which may have an ink layer in the aforementioned step (1) (hereinafter also referred to as "polyester film (A)") may be a simple polyester film without an ink layer, or may have an ink layer formed on the polyester film.

[0053] The aforementioned polyester film preferably has between 75 and 100% of ester repeating units made of ethylene terephthalate units, and ester units. Phthalic acid, isophthalic acid, succinic acid, and adipic acid, and the like, may be suggested as the ester unit acid component that is not ethylene terephthalate. The polyester film may be surfaced treated such as with a corona discharge treatment on the surface in order to improve adhesion with the ink or the adhesive, but not performing a surface treatment is preferable. The film thickness of the polyester film is not particularly restricted, but normally a film thickness of between approximately 5 and 30 μm is preferably used.

[0054] If an ink layer is formed on the polyester film, the ink which forms the ink layer may be an ink used for polyester films, and may be either a thermal hardening or activation beam-hardening ink. The ink may be applied as one color, or by overlaying two or more colors of ink.

[0055] The ink layer may be formed by printing the ink using a gravure printing method, for instance, and if necessary, removing the solvents and hardening by heating or by irradiating with an activation light beam.

[0056] A lamination film for laminating metal plate can be obtained by applying the adhesive of the present invention on to a polyester film (A) (normally on the ink layer surface if the polyester film (A) has an ink layer), and then drying to form an adhesive layer without surface adhesion.

[0057] Application of the adhesive of the present invention onto the polyester film (A) may be performed by a previously known method such as the roller coating method, die coating method, gravure method, gravure offset method, or spray painting method, and normally is applied such that the dry film thickness is between approximately 0.3 and 15 μm, and then the film is dried, for instance, at a temperature between 50°C and 180°C in order to remove the solvents of the adhesive layer.

[0058] In Step (2), the polyester film (lamination film for laminating metal plate) with an adhesive layer that was obtained in Step (1) is rolled into a coil. This coil is stored until used for laminating a metal plate.

[0059] In Step (3), the coil of lamination film for laminating a metal plate obtained in Step (2) is uncoiled and laminated onto the metal plate.

[0060] The aforementioned metal plate which is used for laminating may be, for example, hot rolled steel sheet, cold rolled steel sheet, melted zinc plated steel sheet, electrolytic zinc plated steel sheet, iron-zinc alloy plated steel sheet, zinc-aluminum alloy plated steel sheet, nickel-zinc alloy plated steel sheet, nickel- tin alloy plated steel sheet, tin plate, chrome plated steel sheet, aluminum plated steel sheet, tungsten plated steel sheet, nickel plated steel sheet, stainless steel, tin-free steel, aluminum sheet, copper sheet, titanium sheet, and other metal sheet materials; chemically treated metal sheet made by chemically treating these metal sheets such as with a phosphate treatment, chromate treatment, or a compound oxide film treatment; or painted metal sheet such as a primer painted metal sheet with a primer layer such as a white coat formed on the surface of the aforementioned metal sheet materials or chemically treated metal sheet.

Furthermore, with the present invention, "metal plate" may be a flat sheet like metal plate such as the aforementioned metal sheet materials, chemically treated metal sheet, or primer painted metal sheet, but, for instance, also includes processed metal sheet which has been processed to form, for instance, a can body, or the like.

[0061] The conditions for overlaying the aforementioned metal plate onto the adhesive layer surface of the lamination film for laminating metal plate is not particularly restricted so long as the lamination film for laminating a metal plate is not degraded, the PET film and the metal plate are sufficiently bonded, and a PET laminate metal plate with good appearance is obtained. One example of the overlaying conditions which can be suggested is a method where the temperature of the metal plate is increased to be approximately 120°C to 200°C when thermocompressed using a method which uses a heating roller or a method where the metal plate is a preheated, and then the metal plate and the lamination film for laminating metal plate are thermocompressed for a short period of time (normally less than approximately 2 seconds) and laminated. If a flat metal plate is used, the lamination film for laminating metal plate can be thermally laminated onto one or both sides of the flat metal plate.

[0062] The adhesive layer of the laminated metal plate obtained as described above is hardened by electron beam irradiation, but this electron beam irradiation may be performed either before the flat PET laminated metal plate is formed or after forming. Of course, if the PET laminated metal plate is in the desired shape, the PET laminated metal plate which has been electron beam irradiated will not require forming.

[0063] The accelerator of the electron beam generating source used to irradiate the electron beam may be a Cockcroft accelerator, Cockcroft-Walton accelerator, Van de Graaff accelerator, resonance transformer, transformer, insulated core transformer, Dynamitron, linear fillament, area beam accelerator or high frequency accelerator, or the like. The electron beam energy required to harden the electron beam-hardening adhesive layer is between 100 KeV and 300 KeV, and preferably within a range between 150 KeV and 200 KeV. The irradiation beam intensity is typically between 0.2 Mrad and 15 Mrad, but between 1 Mrad and 5 Mrad is particularly preferable from the viewpoint of the hardness of the adhesive layer and the mechanical strength.

The irradiation time for the electron beam is normally less than approximately 1 second, approximately 1/50th of the time required for thermal hardening.

[0064] The PET laminated metal plate of the present invention is suitably used for metal cans such as cans for beverages, cans for food, cans for miscellaneous, and 5 gallon cans as well as for caps and other metal lid applications, and furthermore, may also be used for thermos bottles, or the outside of home appliances such as refrigerators surfaces.

[0065] PREFFERED EMBODIMENTS

The present invention will be described in further detail using preferred embodiments.

[0066] Hereinafter, both "parts" and "%" are based on a weight standard.

[0067] Manufacture of Polyester Resin (a)

Manufacturing Example 1

0.3 mol of terephthalic acid, 0.55 mol of isophthalic acid, 0.15 mol of sebacic acid, 0.25 mol of ethylene glycol, 0.2 mol of 1,4-butanediol, 0.33 mol of neopentyl glycol, 0.2 mol of 1,4-dimethylol cyclohexane, 0.02 moles of trimethylol propane, and a suitable amount of polymeric condensation catalyst were added to and heated in an autoclave to perform an esterification reaction, and a polyester prepolymer was obtained after a stoichiometric amount of condensation water was removed. 0.25 mol of maleic anhydride was then added to 1 kg of the polyester prepolymer thus obtained, and heated and mixed to perform additional reactions before cooling and adding a solvent blend (toluene/methylethyl ketone = 50/50 (weight ratio)) to obtain a polyester resin (a-1) with 40% solid content.

[0068]

Manufacturing Example 2 through 13

Various polyester resins were obtained in similar manner to Manufacturing Example 1, except that the polybasic acid component, polyhydric alcohol component and an additional acid component were as shown in the following Table 1. Manufacturing Examples 7 through 13 are manufacturing methods of polyester resins for comparison. In Table 1, the formulation amount of acid component and alcohol component are molar quantities, and the formulation amount of the additional acid component is shown as a molar quantity for 1 kg of polyester prepolymer obtained by the esterification of the acid component and the alcohol component.

[0069] The arithmetic mean molecular weight (Mn) weighted mean molecular weight (Mw), Mw/Mn ratio, glass transition temperature (°C) hydroxyl value (KOH mg/g), and acid value (KOH mg/g) for each of the polyester resins obtained in the aforementioned Manufacturing Examples 1 through 13 are shown below in Table 1.

[0070] Table 1

		Manufacturing Examples												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Acid Component (moles)	Terephthalic acid	0.3	0.3	0.3	0.3	0.25	0.3	0.3	0.3	0.3	0.3	0.35	0.25	0.3
	Isophthalic acid	0.55	0.55	0.55	0.55	0.5	0.55	0.55	0.55	0.55	0.55	0.65	0.50	0.55
	Sebacic acid	0.15	0.15	0.15	0.15	0.25	0.15	0.15	0.15	0.15	0.15	--	0.25	0.15
Alcohol Component (moles)	EG	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	1,4-BG	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2
	NPG	0.33	0.33	0.31	0.31	0.33	0.33	0.35	0.33	0.34	0.35	0.33	0.33	0.29
	CHDM	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
	TMP	0.02	0.02	0.04	0.04	0.02	0.02	--	0.02	0.01	--	0.02	0.02	0.06
Additional Acid Component	Maleic anhydride	0.25			0.25	0.25		0.08		0.33	0.08	0.25	0.25	0.08
	Trimellitic anhydride			0.15			0.08							
	Succinic anhydride		0.25											
(mol/kg prepolymer)														
Properties of Polyester Resin	Arithmetic mean molecular weight	20,000	19,000	15,000	17,000	19,000	17,000	20,000	17,000	17,000	9000	18,000	17,000	14,000
	Weighted mean molecular weight	77,000	61,000	66,000	104,000	73,000	56,000	40,000	52,000	59,000	20,000	63,000	61,200	84,000
	(Mw/Mn) ratio	3.8	3.2	4.4	6.1	3.8	3.3	2.0	3.1	3.5	2.2	3.5	3.6	6.0
	Glass transition temperature (°C)	39	39	38	38	23	39	40	39	40	34	65	18	38
	Hydroxyl value KOH mg/g	6	7	9	11	6	11	5	19	1	5	6	5	23
	Acid value KOH mg/g	16	16	20	15	17	9	5	0.6	22	7	6	6	4
Name of Polyester Resin		a-1	a-2	a-3	a-4	a-5	a-6	a-7	a-8	a-9	a-10	a-11	a-12	a-13

[0071] Manufacture of Electron Beam-Hardening Adhesive

Embodiment 1

180 parts of titanium white, 20 parts of body pigment (clay), and an appropriate amount of a solvent blend (toluene/methylethyl ketone = 50/50 (weight ratio)) were added and dispersed in 100 weight parts of a polyester resin (a-1) solution with a solid content of 40% obtained in Manufacturing Example 1, this dispersion was then blended with 137.5 parts of the aforementioned polyester resin with a solids content of 40% (55 parts based on solid content), 5 parts of "Aronix M-315" (product of Toagosei Co. Ltd., polyester containing polymeric unsaturated groups, polymeric unsaturated double bond concentration approximately 7.0 mol/kg, arithmetic mean molecular weight approximately 420, essentially no hydroxyl value), 25 parts (20 parts based on solid content) of "Duranate TPA-B80X" (product of Asahi Kasei, hexamethylene diisocyanate type blocked polyisocyanate compound, solid content 80%), and 3 parts of "Duranate TPA100" (product of Asahi Kasei, hexamethylene diisocyanate polyisocyanate compound) and methylethyl ketone to make an electron beam-hardening adhesive with a solid content of 50%.

[0072] Embodiments 2 ~ 12 and Comparative Examples 1 ~ 11

Various electron beam-hardening adhesives were obtained by the same manner as Embodiment 1, except that the formulation composition was as shown in the following Table 2. The formulation amounts of each of the components in Table 2 are expressed in solid weight units. In Table 2, the (Notes) have the following meanings.

[0073] (*1) EB-450: Product of UCB S. A. Specialty Chemicals, polyester oligomer with polymeric unsaturated groups, polymeric unsaturated double bond concentration of approximately 4 mol/kg, arithmetic mean molecular weight of approximately 1500, and a hydroxyl value of 50 KOH mg/g.

[0074] (*2) Aronix M-8100: Product of Toagosei Co., Ltd., polyester oligomer with polymeric unsaturated groups, polymeric unsaturated double bond concentration of approximately 6.7 mol/kg, arithmetic mean molecular weight of approximately 600, and essentially no hydroxyl groups.

[0075] Manufacture of PET Laminated Metal Plate

Each of the electron beam-hardening adhesives obtained from Embodiments 1 through 12 and Comparative Examples 1 through 11 were applied to a dried film thickness of approximately 3 µm using gravure application onto the corona discharge treated surface of ester film E-5100 (polyester film with a film thickness of 12 µm) (corona discharge treated on one side) produced by Toyobo Co. Ltd. The film was then passed through a drying oven at 100°C for 10 seconds to evaporate off the solvent component. The polyester film with adhesive applied was tested for adhesive layer surface tackiness, and blocking resistance based on the following test methods. These test results are shown in the following Table II.

[0076] This polyester film with adhesive applied was thermally laminated onto Canlite (product of Nippon Steel Corp. which is a 0.19 mm thick tin plate, at a roller temperature of 180°C and a roller pressure of 5.0 kg/cm2. Then, an electron beam was irradiated through the polyester film of the laminated metal plate at a current of 50 mA, an intensity of 4 Mrad, and an acceleration voltage of 270 KeV using an electron beam accelerator to harden the adhesive layer in order to obtain each of the PET laminated metal plates.

[0077] The PET laminated metal plate obtained as shown above was tested for the surface appearance and retort resistance adhesion of the laminated polyester film based on the following test methods. These test results are shown in Table 2.

[0078] Test Items

Tackiness: The adhesive coated surfaces of two adhesive coated polyester films obtained by evaporating off the solvent component (approximately 10 seconds after removing from the drying oven) were overlaid and sufficiently compressed by hand, and then the two films were pulled apart and evaluated for the area of peeling on the side of the two adhesive coated surfaces which had the larger area of peeling of adhesive from the polyester film.

(O): absolutely no peeling was observed on either of the two adhesive coated surfaces.

O: Peeling was observed and the area of peeling on the larger side was less than 10%.

☐: The area of peeling of the larger side was 10% or larger but less than 30%.

X: The area of peeling of the larger side was 30% or more.

[0079] Blocking resistance: A surface, formed by corona discharge treating a separate "Ester Film E5100" and then forming a epoxy-polyester overcoat paint film on the treated surface, was overlaid facing the surface of the adhesive on the surface of an adhesive coated polyester film obtained by evaporating the solvent component, a 10 kg/cm^2 pressure was applied, and the film was stored in a room at a temperature of 25°C and a relative humidity of 60%RH for three days. The stored laminated film was cut to a width of 30 mm, and the peeling strength (g/30 mm wide) was measured when the separate PET film was peeled from the dried film surface at an angle of 180 degrees at a peel speed of 500 mm/minute, and an evaluation was performed according to the following criteria.

(O): Peel strength is less than 10 g/30 mm wide
O: Peel strength is 10 g/30 mm wide or higher but less than 20 g/30 mm wide
□: Peel strength is 20 g/30 mm wide or higher but less than 50 g/30 mm wide
X: Peel strength is 50 g/30 mm wide or higher

[0080] Film surface appearance: Using the same laminate prepared for the aforementioned blocking resistance test, a different PET film which had been placed on the dried coated surface was peeled from the laminate film after storage for two days and four days at room temperature, and a 0.2 mm thick tin plate was laminated onto the dried film surface obtained at a lamination temperature of 160°C, linear pressure of 50 kg, and speed of 200 m/minute, and the appearance of the PET laminate surface of the PET laminated metal plate obtained was evaluated according to the following criteria.

(O): No problems were observed in the PET laminate surface
O: Slight orange peel surface observed on the PET laminate surface
□: Moderate orange peel surface observed on the PET laminate surface
X: Severe orange peel surface observed on the PET laminate surface.

[0081] Laminate strength: the PET laminate metal plate prepared for the aforementioned appearance test of the film surface was cut to a 15 mm width (laminate storage period 24 hours), and a peel test was performed between the PET film and the tin plate, and the difficulty of peeling was evaluated according to the following criteria.

(O): PET film did not peel at all
O: A part of the PET film peeled, but the PET film broke before the peel length reached 5 mm
□: A part of the PET film peeled, but the PET film broke when the peel length was 5 mm or longer, but less than 20 mm
X: The PET film peeled and the PET film peeled completely off or broke at a peel length of 20 mm or longer.

[0082] Retort resistance adhesion in the formed region: The PET laminate metal plate prepared for the aforementioned film surface appearance test was pressed with the tin plate side facing up in a 200 Endo forming apparatus (can lid forming machine), the can with lid that was created was subjected to retort processing in steam at 125°C for 30 minutes, and the peeling condition of the PET film was evaluated according to the following criteria.

(O): Absolutely no peeling of the PET film was observed
O: Slight peeling of a part of the PET film in the circumferential region
□: Moderate peeling of a part of the PET film in the circumferential region
X: Peeling around the whole circumferential region of the PET film

[0083] Table 2

			Comparative Examples											
			1	2	3	4	5	6	7	8	9	10	11	12
Polyester resin (a)	Type		a-1	a-1	a-1	a-1	a-1	a-1	a-1	a-2	a-3	a-4	a-5	a-6
	Amount (parts)		95	90	80	95	90	90	90	90	90	90	90	90
Polymeric unsaturated oligomer (b)	Aronix M-315		5	10	20		5		10	10	10	10	10	10
	EB-450 (*1)					5	5							
	Aronix M-8100 (*2)							10						
Blocked polyisocyanate			20	10	--	5	5	10	15	5	5	5	5	5
Unblocked polyisocyanate			3	5	7	5	5	5	5	5	5	5	5	5
Titanium white			180	180	180	180	180	180	180	180	180	180	180	180
Body pigment			20	20	20	20	20	20	20	20	20	20	20	20
Test Results	Adhesion		(O)	(O)	O	(O)	(O)	O	O	(O)	(O)	(O)	(O)	(O)
	Blocking resistance		(O)	(O)	O	(O)	(O)	O	O	(O)	O	(O)	O	(O)
	Appearance of film surface	2 days after application	O	(O)	(O)	(O)	(O)	(O)	O	(O)	(O)	(O)	O	(O)
		4 days after application	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)
	Laminate strength		O	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)
	Retort adhesion in formed region	2 days after application	(O)	(O)	(O)	O	O	(O)	(O)	(O)	(O)	(O)	(O)	(O)
		4 days after application	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)

[0084] Table 3

Table 2 (Continued)

			1	2	3	4	5	6	7	8	9	10	11
Polyester resin (a)	Type		a-1	a-1	a-1	a-2	a-7	a-8	a-9	a-10	a-11	a-12	a-13
	Amount (parts)		98	75	90	100	90	90	90	90	90	90	90
Polymeric unsaturated oligomer (b)	Aronix M-315		2	25	10		10	10	10	10	10	10	10
	EB-450 (*1)												
	Aronix M-8100 (*2)												
Blocked polyisocyanate			10	--	10	5	5	5	5	5	5	5	5
Unblocked polyisocyanate			5	3	12	5	5	5	5	5	5	5	5
Titanium white			180	180	180	180	180	180	180	180	180	180	180
Body pigment			20	20	20	20	20	20	20	20	20	20	20
Test Results	Adhesion		(O)	□	□	(O)	X	O	X	X	O	□	O
	Blocking resistance		(O)	□	X	(O)	X	(O)	(O)	X	(O)	X	(O)
	Appearance of film surface	2 days after application	(O)	□	(O)	(O)	X	□	□	X	(O)	□	(O)
		4 days after application	(O)	O	(O)	(O)	□	O	□	X	(O)	O	(O)
	Laminate strength		□	(O)	(O)	X	O	O	O	□	□	O	O
	Retort adhesion in formed region	2 days after application	X	□	(O)	□	X	□	□	X	X	O	X
		4 days after application	□	□	(O)	□	□	□	□	X	X	(O)	X

[0085] EFFECT OF THE INVENTION

By using the adhesive of the present invention, an excellent adhesive layer can be formed which can be used for a long period of time, and the polyester film which forms the adhesive layer has favorable blocking resistance toward the adhesive layer, and the adhesion to the metal plate is excellent.

[0086] Furthermore, the PET laminate metal plate made by laminating a polyester film formed with this adhesive layer will have excellent appearance on the PET film surface, as well as excellent forming properties and retort resistance, and the like.

[0087] The PET laminate metal plate which uses the adhesive of the present invention can be favorably used for can applications such as the inside and outside surface of the can.